

U.S. Patent Application Serial No. 10/829,010
Reply to Office Action of January 4, 2007

REMARKS

Claims 17-73 were previously pending in the application. Claims 17-19, 22-69, and 72-73 are canceled. Claims 20-21 and 70-71 remain pending in the present application. No new matter is entered, and the amendments made herein are fully supported by the specification, claims and drawings as originally filed.

Claims 20, 48, 49, 70 and 71 are objected for reciting "%" rather than "wt. %" as per the specification. Claims 48 and 49 are cancelled. Claims 20, 70 and 71 are amended as suggested in the Office Action. Applicants request that the objection be withdrawn.

The Examiner rejected claims 17-19, 30-44, 47, 50-66, 69 and 72-73 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent No. 6,607,620 to Knickerbocker et al. in view of U.S. Patent No. 5,130,067 to Flaitz et al. Applicants traverse the rejection to the extent that it can be maintained. As these claims have been canceled, this rejection is rendered moot.

The Examiner rejected claims 20-21 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent No. 6,607,620 to Knickerbocker et al. in view of U.S. Patent No. 5,130,067 to Flaitz et al. as applied to claim 19, and further in view of JP 49-37921. Applicants traverse the rejection to the extent that it can be maintained.

Independent claim 20 and dependent claims 21, 70 and 71 relate to a method for reducing shrinkage during sintering low temperature co-fired ceramics. A layer to constrain shrinkage in the X-Y direction is positioned on a dielectric body to enclose an active area. The constraining layer is a low sintering temperature material comprising a strong auxiliary component to lower the sintering temperature of the layer. Bonding glass may be used to bond the constraining layer to the ceramic layer. Sintering involves bonding of adjacent surfaces of a mass of particles by heating below the fusion temperature. In sharp contrast, glass formation involves heating of glass-forming materials to produce a completely fused melt that is cooled to a non-crystalline molecular structure. Applicants enclose a page from A. Dodd and D. Murfin, "Dictionary of Ceramics", The Institute of Materials (1994); and two pages from W. Kingers, H. Bowen, and D. Uhlmann, Introduction to Ceramics, John Wiley & Sons (1991).

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Knickerbocker et al. disclose a method for constraining shrinkage during processing of greensheets prior to sintering. Knickerbocker et al. apply a constraining frame that may be a glass ceramic material. Knickerbocker et al. fail to teach a constraining frame comprising a low sintering temperature material. As explained above, sintering involves forming an agglomeration of particles, whereas glass ceramic is a non-crystalline material. Applicants respectfully submit that glass ceramic does not suggest a mass of agglomerated particles. Further, the constraining frame is cut away before sintering the greensheets and therefore does not affect shrinkage during sintering (column 4 lines 36-53).

Flaitz et al. disclose a process for controlling Z-direction camber and X-Y bulge and distortion by applying pressure to the surface of a green ceramic structure during sintering. Flaitz et al. disclose several embodiments of their invention including the use of "contact sheets" that rely on friction to control shrinkage (beginning at column 8 line 65). The contact sheets must not fuse to the ceramic and are removed from the ceramic after sintering. There is no teaching or suggestion by Flaitz et al. of a process that controls shrinkage during firing of a monolithic structure that includes bonding glass applied between the contact sheet (constraining layer) and the ceramic layer (dielectric body). The combination Knickerbocker et al. and Flaitz et al. fail to teach or suggest a constraining layer (frame) comprising a low sintering material that is present during sintering; and fail to teach or suggest a strong auxiliary component to lower the sintering temperature of the constraining layer.

JP '921 is cited for teaching that glass can be strengthened by the presence of vanadium oxide. The Office Action concludes that it would be obvious to one of ordinary skill to similarly modify sintered powder. JP '921 also states that the presence of vanadium oxide provides glass having low expansibility, whereas the claimed sintered constraining layer reduces shrinkage of a ceramic substrate (paragraph [0043]). As explained by the "Dictionary of Ceramics" and the Introduction to Ceramics cited above, glass is a non-crystalline solid. It is usually formed from a melt. Because of a rapid cooling rate, glass has not enough time to form a long range ordered crystalline structure. Therefore, it is a non-crystalline solid. In sharp contrast, vanadium oxide in the present invention directly functions as a sintering aid to lower sintering temperature of refractory ceramics (page 12, paragraph [0037] and [0044]). Vanadium oxide is a crystalline material as opposed to non-crystalline glass. Vanadium oxide has a melting point of about 690°

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C. After melting, it acts as a liquid phase to enable a liquid phase sintering. There is no reasonable expectation that a substance useful for modifying the physical properties of non-crystalline glass would provide a similar modifying effect on the physical properties of sintered particles. No art is cited that establishes that vanadium oxide performs an equivalent function in materials as physically and chemically diverse as glass and sintered powder. Factual findings, fully explained, to support the conclusions of the Office Action must be provided. See *In re Lee*, 61 USPQ2d 1430 (Fed. Cir. 2002).

Applicants respectfully submit that Knickerbocker et al. in view of Flaitz et al. and further in view of JP 49-37921 does not teach or suggest all of the elements of the invention as claimed, and request that the rejection on this ground be withdrawn.

The Examiner rejected claims 45-46 under Section 103(a) as being unpatentable over U.S. Patent No. 6,607,620 to Knickerbocker et al. in view of U.S. Patent No. 5,130,067 to Flaitz et al. as applied to claim 17, and further in view of U.S. Patent No. 6,488,795 to Sakai. Applicants traverse the rejection to the extent that it can be maintained. As these claims have been canceled, this rejection is rendered moot.

The Examiner rejected claims 47-49 under Section 103(a) as being unpatentable over U.S. Patent No. 6,607,620 to Knickerbocker et al. in view of U.S. Patent No. 5,130,067 to Flaitz et al. as applied to claim 17, and further in view of JP 2001-158670. Applicants traverse the rejection to the extent that it can be maintained. As these claims have been canceled, this rejection is rendered moot.

The Examiner rejected claims 67-68 under Section 103(a) as being unpatentable over U.S. Patent No. 6,607,620 to Knickerbocker et al. in view of U.S. Patent No. 5,130,067 to Flaitz et al. as applied to claim 19, and further in view of JP 58-115838 Abstract. Applicants traverse the rejection to the extent that it can be maintained. As these claims have been canceled, this rejection is rendered moot.

Claims 21, 70 and 71 depend directly or indirectly from claim 20. As explained above, claim 20 is now allowable over the combined art relied on in the Office Action. Because this

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amendment places the claims into condition for allowance, and raises no new issues, consideration and entry of this Amendment After Final is appropriate.

In view of the above amendments and remarks, Applicants respectfully request a Notice of Allowance. If the Examiner believes a telephone conference would advance the prosecution of this application, the Examiner is invited to telephone the undersigned at the below-listed telephone number.

Respectfully submitted,



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From A. D. F. and D. Murray, "Dictionary of Ceramics", The Institute of Materials

Gersley Borate. A sodium-calcium borate produced at the Gersley Mine, Death Valley, California (U.S. Borax and Chemical Corp., Los Angeles).

Getting. The actual process of digging clay, by hand or by excavator, getting and transporting form the successive stages of winning.

Gibbsite. Aluminum trihydrate, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. Occurs in Dutch Guiana, the Congo, and some other areas where laterization has occurred. A typical analysis is 65% Al_2O_3 , 13% H_2O and 2% impurities, but many samples contain clay. Gibbsite requires calcination at a very high temperature to eliminate all the shrinkage that results from the loss of water.

GLASS AND DILATATIONAL FACTORS. See INTERNAL EXPANSION FACTORS FOR GLASS.

Glaze. The painting of pottery with liquid glass, this is subsequently fired on at about 700°C.

Gillmore Needle. Apparatus for the determination of the initial and final set of portland cement (Q. A. Gillmore, *Practical Treatise on Limes, Hydromic Cement and Mortars*, New York, 1841). The present form of apparatus consists of two tanged rods which slide vertically in a frame; the rod ('needle') for the determination of initial set is 1/8 in. (2 mm) dia. and weighs 1/8 lb (110g), the needle for the final set is 1/8 in. (1 mm) dia. and weighs 1/8 lb (40g). Details are given in ASTM C-266 (cf. VICKAR VERSPIKE).

Glimmer. Term in the N. Staffordshire potteries for a person who grinds from chisels-ware, after it has been taken from the glaze kiln, any adhering particles of refractory material from the kiln furniture; cf. SOKING. (From *Gimnet*, an old term for a tool used by carpenters to remove excrescences from wood.)

Glazier. Term that has been used in USA for devitrified glass products of the type exemplified by PYROKERAM (q.v.).

GLAZIMETER. See INFRASOUND GLAZIMETER.

Glastol. Trade name. Acrylic copolymer used as sealers for porous glazes and as media for coloents. (Allied Colloids, UK).

Glas-Jot. Trade name. A glass-fibre joint for clay sewer pipes. (Portman Pipe, USA).

Glass. A solid with no long-range order in the arrangement of its atoms. ASTM C162-92 defines a glass as an inorganic product of fusion that has cooled to a rigid condition without crystallizing, and notes that glasses are typically hard and brittle, with a conchoidal fracture. The word is used loosely as a synonym for GLASSWARE (q.v.). The Annual Book of ASTM Standards, Vol 15.02 lists over fifty test methods and property requirements for glass and glass

products. The names of many types of glass indicate their main constituents, e.g. soda-lime glass (the presence of silica being understood); for the system of designating types of optical glass see OPTICAL GLASS CLASSIFICATION. A major advance in the understanding of the fundamental nature of a glass was made when W. H. Zachariasen (*J. Amer. Chem. Soc.*, 54, 3841, 1932) deduced that the characteristic properties of glasses are explicable if the interatomic forces are essentially the same as in a crystal, but in the three-dimensional atomic network in a glass lacks the symmetry and periodicity of the crystalline.

NOVERIK. Zachariasen's rules for the formation of an oxide glass are (1) the sample must contain a high proportion of cations that are surrounded by oxygen tetrahedra or by oxygen triangles; (2) these tetrahedra or triangles must share metallic oxides, or salts, and low-melting

only corners with each other; (3) some oxygen atoms must be linked to only two such cations and must not form further bonds with any other cations. The ions in a glass are thus divided into NETWORK-FORMING (q.v.) and NETWORK-MODIFYING (q.v.). See also STRUCTURE, VITRON. See also HALIDE GLASSES, CHALCOGENIDE GLASSES.

Glassblowing. Shaping hot glass by air pressure. This may be done by hand and mouth by a craftsman *glassblower*, or may be an element of various forming processes; see BLOW-AND-THLOW, PRESS-AND-BLOW, PUFF-AND-THLOW.

Glass-bonded Fibre. See VITRA (GLASS-BONDED).

Glass-Ceramic. A type of ceramic material that, while in the form of a molten glass, is shaped by one of the conventional glassmaking processes, and is subsequently devitrified in a controlled manner so that the finished product is crystalline. The crux of the process is the precipitation, during cooling of the shaped ware, of nucleating areas previously added in small amounts to the glass batch; the nucleated article is then heated to a temperature at which the nucleated crystals can grow. Devitrified-glass products can be made in a wide range of compositions; the properties can thus be varied, but typically the ware is impermeable and has high strength and good thermal-shock resistance. Uses include RAFTERS (q.v.), HIGH-TEMPERATURE bearings, thread guides and domestic ovenware. (See also NEO-CERAMIC GLASS).

Glass-coated Steel or Glass-lined Steel. A grade of vitreous enameled ware that has good resistance to chemical attack at high temperatures and pressures; also known as *Glassed Steel*. *Glassed* Enamel. A mixture of coloured metallic oxides, or salts, and low-melting

flux, e.g. lead borosilicate, used for the decoration or labelling of glass-ware; the enamel is fired-on at a red heat.

Glass-encapsulated Wiring. See ENCAPSULATED WIRING.

Glass Eye. A large unbroken blister on vitreous glass-ware.

Glass Fibre. Fibreous glass made by mechanical drawing or centrifugal spinning, or by the action of a blast of air or steam to produce *Single Fibre*. The unprocessed filaments are known as *Basic Fibre*; a number of filaments bound together form a *Fibrill*. Long glass fibres are known as 'SEK', a fibre-like mass of fibres is 'Waf'; felt-like material is 'Mer'. Formerly glass (or material) was produced as matbles which were remelted in an electric furnace to form filaments. Nowadays the *discontinuous method* is used. Fibres are drawn directly from holes in an alloy bush, at winding speeds of 50 m/s. The Owens STEAM-QUENCHED process (q.v.) is used to make glass wool. Glass filaments are a few micrometres in diameter, and much stronger than ordinary glass because free of surface flaws. There are over 20 British Standards for glass fibre products and plastics and cement products with glass fibre reinforcement.

Glass Frost. Very thin glass that has been crushed for use as a decorative material (cf. *TESSERA*).

Glass-knocker Ceramics. Translucent dental cements, made by the reaction between aluminum silicate glass powder, and polyacrylic acid polymers or acrylic acid. Developed by A. D. Wilson and B. E. Kent at the Laboratory of the Government Chemist, *J. Appl. Chem. Biotechnol.* 21, (11), 315, 1971. For specification, see B.S. 6639.

Glassification. Passivation of semiconductor devices by complete encapsulation in glass. An American

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(c) Silicates have structures in which SiO_4^{4-} tetrahedra share vertices to form chains, rings, sheets, etc. In phosphates (PO_4^{3-}) and sulfates (SO_4^{2-}) similar tetrahedra are found, but they are always isolated. Yet AlPO_4 has a structure which corresponds to that of quartz, SiO_2 .

(d) The alkaline earth oxides, MgO , SrO , BaO , all have the rock salt structure. The hardness and melting points of the compounds decrease in the order given.

(e) MgO (rock salt structure) and Li_2O (fusilite structure) both are based on cubic close-packed oxygen, with cations occupying interstices in the array. Yet predominant point defect in MgO is of the Schottky type: that in Li_2O is of the Frenkel type.

1.11. The garnets, $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_12$ and $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_12$, are isomorphous in a manner similar to Fe_2SiO_4 and Mg_2SiO_4 . They are not isomorphous with $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_12$, and neither is Mg_2SiO_4 or Fe_2SiO_4 isomorphous with Ca_3SiO_4 . Give an explanation for this based on ionic size and coordination number. On the basis of your theory predict a mineral not mentioned in this question that will be isomorphous with Mg_2SiO_4 , one for Ca_2SiO_4 , one for $\text{Mg}_2\text{Al}_2\text{Si}_3\text{O}_12$, and one for $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_12$.

1.14. A certain engineer was asked to identify some rhomb-shaped crystals that had crystallized from a glass melt. The X-ray diffraction pattern showed they were a single phase (only one kind of crystal structure), but the chemical analysis indicated a complicated formula $\text{K}_2\text{AlF}_6\text{Al}_2\text{O}_5\text{Al}_2\text{Si}_5\text{O}_10$ on an empirical basis. If he called you in as a consultant, would you be able to show him this is related to muscovite (potassium mica) and to the feldspar (potassium feldspar)? Show what substitutions in talc or phlogopite that have been made to produce this crystal.

From W. Kingery, H. Bowen, D. Uhlmann, "Introduction to Ceramics," John Wiley & Sons

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19.1

Structure
of
Glasses

Even though a majority of natural and manufactured solids are crystalline in nature, as discussed in Chapter 2, materials which are not crystalline are of great importance for both traditional and newly developed ceramics. One important class is the liquid silicates, the properties of which are an essential part of the ceramist's knowledge in the formulation of glasses, glazes, and enamels. Solid glasses, of which the silicates are the technologically most important group, usually have a more complex structure than the liquids from which they are derived, and recent studies indicate a complexity which is still not well understood, although the broad structural characteristics seem reasonably clear. A more newly developed class of materials is thin films deposited as nanocrystalline solids from the vapor phase, sheet which even less is known as to structural details. In each of these classes of ceramic materials the short-range order is preserved in the immediate vicinity of any selected atom, that is, the first coordination ring; the longer-range order characteristic of the ideal crystal is dissipated in a way characterized by diversity among different systems and by difficulty in precise description.

We focus our attention on glasses, which are by far the most important group of inorganic noncrystalline solids. The structure of glasses may be considered on three scales: (1) the scale of 2 to 10 Å, or that of local atomic arrangement; (2) the scale of 30 to a few thousand nanometers, or that of submicrostructure; and (3) the scale of microns (in millimeters or more), or that of microstructure and macrostructure. In this chapter we consider the atomic structure and the submicrostructure of glasses; the consideration of microstructural features is deferred to Chapter 11.

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3.1 Glass Formation

Glasses are usually formed by solidification from the melt. The structure of glasses can be clearly distinguished from that of liquids, since glass structure is effectively independent of temperature. This can best be seen by a plot of the specific volume of the crystal, liquid, and glass as a function of temperature (Fig. 3.1). On cooling the liquid, there is a discontinuous change in volume at the melting point if the liquid crystallizes. However, if no crystallization occurs, the volume of the liquid decreases at about the same rate as above the melting point until there is a decrease in the expansion coefficient at a range of temperature called the glass transformation range. Below this temperature range the glass

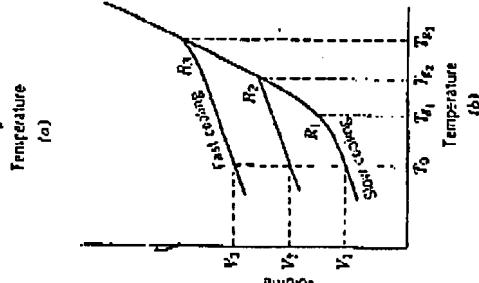
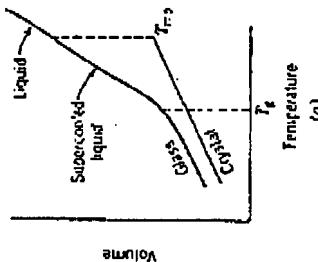


Fig. 3.1. Schematic specific volume-temperature relations: (a) Relations for liquid, glass, and crystal; (b) glasses formed at different cooling rates $R_1 < R_2 < R_3$.

STRUCTURE OF GLASSES

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structure does not relax at the cooling rate used. The expansion coefficient for the glassy state is usually about the same as that for the crystalline solid. If slower cooling rates are used so that the time available for the structure to relax is increased, the supercooled liquid persists to a lower temperature, and a higher-density glass results. Similarly, by heating the glassy material in the annealing range, in which slow relaxation can occur, the glass structure in time approaches an equilibrium density corresponding to the supercooled liquid at this temperature.

A concept useful in discussing the properties of glasses is the glass transition temperature T_g , which corresponds to the temperature of the intersection between the curve for the glassy state and that for the supercooled liquid (Fig. 3.1). Different cooling rates, corresponding to different relaxation times, give rise to a different configuration in the glassy state equivalent to different points along the curve for the supercooled liquid. In the transition range the time for structural rearrangements is similar in magnitude to that of experimental observations. Consequently the configuration of the glass in this temperature range changes slowly with time toward the equilibrium structure. At somewhat higher temperatures the structure corresponding to equilibrium at any temperature is achieved very rapidly. At substantially lower temperatures the configuration of the glass remains sensibly stable over long periods of time.

In discussing the structural characteristics of glasses, reference is often made to the structure of a particular glassy material. It should be noted, however, that any determination of glass structure is only meaningful within limits set from the volume-temperature relations shown in Fig. 3.1. As the liquid is cooled from a high temperature without crystallizing, a region of temperature is reached in which a bend appears in the volume-temperature relation. In this region, the viscosity of the material has increased to a sufficiently high value, typically about 10^7 to 10^8 poise, so that the sample exhibits solidlike behavior. As shown in Fig. 3.1b, the glass transition temperature increases with increasing cooling rate, as do the specific volumes of the glasses which are formed. In the case shown, the specific volume of the glass at temperature T_g can be V_1 or V_2 or V_3 , depending on which of the three cooling rates was used in forming the glass. The maximum difference in specific volume obtainable with variations in the cooling rate is typically in the range of a few percent; only within this range can one speak of the structure of a glass without carefully specifying its mode of formation.

Noncrystalline solids can be formed in other ways besides cooling from the liquid state, and their structure may differ significantly from glasses formed by the cooling of liquids. Among these alternative methods, the